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(54) Dielectric material comprising Ta2O5 doped with TiO2 and devices employing same

(57) Applicant has discovered that the dielectric constant of Ta_2O_5 can be significantly enhanced by the addition of small quantities of TiO_2. Specifically, if Ta_2O_5 is doped with more than about 3 mole percent of TiO_2 the doped material will have a dielectric constant higher than the undoped material. For example, at a ratio of 0.92 Ta_2O_5:0.08 TiO_2, the dielectric constant is enhanced by a factor of more than three. Because both Ta and Ti are compatible with current microelectronics processing, the new dielectric can be used to make capacitors of reduced size with but minor modifications of conventional processes.

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Description

Field of the Invention

This invention relates to dielectric materials and, in particular, to dielectric materials comprising Ta_2O_5 doped with TiO_2 to enhance their dielectric constants. These materials are particularly useful for providing dielectric layers in capacitors.

Background of the Invention

As microelectronic circuits become increasingly integrated, the demand for smaller components becomes stronger. For the capacitive components, the materials presently employed have inadequate dielectric constants to be used with lower area. To remedy this problem, exotic high dielectric constant materials such as Barium Strontium Titanate (BST) are presently in the research stage in many laboratories, especially for their potential use in DRAM applications. Such materials, however, invariably require the use of chemical elements foreign to the usual microelectronics manufacturing procedures and therefore require alteration of manufacturing processes and extensive compatibility testing. Accordingly, there is a need for a new improved dielectric material compatible with conventional microelectronic processing.

Summary of the Invention

Applicant has discovered that the dielectric constant of Ta_2O_5 can be significantly enhanced by the addition of small quantities of TiO_2. Specifically, if Ta_2O_5 is doped with more than about 3 mole percent of TiO_2 the doped material will have a dielectric constant higher than the undoped material. For example, at a ratio of 0.92 Ta_2O_5 : 0.08TiO_2, the dielectric constant is enhanced by a factor of more than three. Because both Ta and Ti are compatible with current microelectronics processing, the new dielectric can be used to make capacitors of reduced size with but minor modifications of conventional processes.

Brief Description of the Drawings

The advantages, nature and various additional features of the invention will appear more fully upon consideration of the illustrative embodiments now to be described in detail in connection with the accompanying drawings. In the drawings:

FIG. 1 is a graphical illustration of the dielectric constant at 1 MHz of $(Ta_2O_5)_{1-x}$ $(TiO_2)_x$ at 20°C.

FIG. 2 is a graphical illustration of the dielectric constant at 1 MHz of $(Ta_2O_5)_{0.92}$ $(TiO_2)_{0.08}$ at various temperatures.

FIG. 3 shows the variation of the dielectric constant with temperature for several different compositions of doped Ta_2O_5.

FIG. 4 is a schematic cross section of a capacitor comprising a dielectric layer of Ta_2O_5 doped with TiO_2.

It is to be understood that these drawings are for purposes of illustrating the concepts of the invention and, except for the graphs, are not to scale.

Detailed Description

Applicant has found that the dielectric constant of Ta_2O_5 is enhanced by small quantities of TiO_2 dopant It was determined that the dielectric constant K of $(Ta_2O_5)_{1-x}$ $(TiO_2)_x$ exceeds that of undoped Ta_2O_5 for $x \leq 0.03$. K is doubled over the approximate range $0.05 < x < 0.15$, and it achieves a maximum of more than three times the undoped value at $x \simeq 0.08$. The remaining discussion is divided into three parts. Part A describes preparation of the bulk material. Part B describes its properties, and Part C shows its use in making improved capacitors.

A. Material Preparation

In a series of experiments, ceramic samples in the Ta_2O_5-TiO_2 chemical system were made by standard ceramic processing techniques. High purity tantalum oxide and titanium oxide were first mixed in a predetermined molar ratio, mechanically ground, and fired for several nights in dense Al_2O_3 crucibles in air between 1350 and 1400°C with intermediate grinding. The powders were then pressed into 0.5 inch diameter pellets approximately 0.125 inch thick and fired in air on powder of their own composition for 16-24 hours at 1400°C. They were cooled to 100°C at 200°C/hr. before the furnace was turned off.

B. Properties

Surfaces of the pellets were then sanded smooth and 1:1 mole ratio Ga:In alloy solder electrodes were applied. Measurements of the dielectric constants and dissipation factors were then made at 1 MHz and 100 KHz using an HP4192A impedance analyzer. The data for the 1 MHz measurements is summarized in Table 1. The dielectric constant, dissipation factor, total variation in dielectric constant, and temperature coefficient of dielectric constant (TCK) in a -20 to 60°C temperature range are tabulated for each composition studied.

Table 1. Dielectric Properties of Bulk Polycrystalline $Ta_2O_5-TiO_2$ Ceramics Measured at 1 MHz

Composition Ta_2O_5	TiO_2	K† at 20°C	D‡ at 20°C	Total Change in K(%) -20 to + 60°C	TCK* ppm/°C
1.00	0.00	35.4	0.006	+4.8	600
0.98	0.02	20.3	0.016	+7.6	950
0.96	0.04	46.6	0.038	+20.6	2580
0.94	0.06	94.0	0.016	+22.5	2810
0.92	0.08	126.2	0.010	+23.4	2930
0.90	0.10	97.8	0.026	+24.3	3040
0.875	0.125	88.6	0.008	+16.9	2110
0.85	0.15	69.1	0.008	+13.0	1620
0.80	0.20	59.4	0.009	+11.4	1420
0.70	0.30	57.6	0.021	+12.1	1510
0.60	0.40	42.2	0.009	+9.7	1210

† K = dielectric constant
‡ D = dissipation factor (=tan δ)
* TCK = temperature coefficient of dielectric constant
= total change in K (in ppm)/80°C

FIG. 1 plots the dielectric constant K at 1 MHz and 20°C for various compositions of $(Ta_2O_5)_{1-x}(TiO_2)_x$. As can be seen, K drops for low level doping of TiO_2 less than about 3 mole percent and thereafter increases over that of the undoped material. The greatest enhancement of K occurs at compositions between 5% TiO_2 and 15% TiO_2 where K more than doubles. The graph shows a strong peak of K=126 at about 8% TiO_2 doping. As the TiO_2 component increases beyond about 40% it becomes increasingly difficult to form films of the material with enhanced properties. Similar behavior was observed at 100 KHz.

FIG. 2 plots the temperature dependent dielectric constant for a 0.92 Ta_2O_5:0.08 TiO_2 polycrystalline pellet. The increased dielectric constant that results from TiO_2 doping of Ta_2O_5 is accompanied by a significant increase in TCK.

FIG. 3 plots the temperature variation of K for several compositions. The graph shows that materials near the highest K have similar TCKs. It also shows that an enhancement of the dielectric constant by a factor of 2 over Ta_2O_5 with lower TCK than the 0.92:08 material is possible for compositions near 85% Ta_2O_5. The composition region between approximately 94 and 88% Ta_2O_5 yields the best materials if the value of K is the primary consideration.

Characterization of the materials by conventional powder X-ray diffraction (CuK x-radiation) showed that the enhanced dielectric constant for 8%-15% TiO_2 doping is associated with the presence of the H' monoclinic Ta_2O_5 solid solution phase. Thus the TiO_2 doping resulted in the formation of a crystallographic phase different from that obtained in pure Ta_2O_5.

Table 1 also shows the values of the dielectric dissipation (D) at 1 MHz. Unlike the other dielectric data, the D values do not systematically change with composition. This suggests that the loss values are dominated by uncontrolled parameters in the present processing procedure, such as the presence or absence of oxygen vacancies, well known to occur in titanium based oxides. In any case the dissipation factor measured for the 0.92:0.08 composition is not more than a factor of 2 higher than that for pure Ta_2O_5, and may actually be of the same magnitude as that of Ta_2O_5 in properly processed materials, as is suggested by the lower D values for other materials in the table.

C. Exemplary Device Application

FIG. 4 is a schematic cross section of a capacitor 10 comprising a dielectric layer 40 of TiO_2 doped Ta_2O_5 disposed between a pair of electrodes 41 and 42. In preferred applications electrode 41 is supported on a substrat 43 containing other microelectronic components (not shown) and layer 40 is preferably $(Ta_2O_5)_{1-x}(TiO_2)_x$ where $0.03 \leq x \leq 0.4$ and preferably $0.05 \leq x \leq 0.15$. A thin film of the dielectric can be deposited on electrode 41 from the bulk material by conventional sputtering or laser ablation processes. Preferred electrodes can be made of doped polysilicon. The advantage of using this dielectric material is that because of its enhanced dielectric constant, the area on the substrate consumed by the capacitor can be reduced, thereby permitting a higher density of components. Use of material with $x \approx 0.08$ permits the same capacitance in one-third the area as that for $x=0$.

It is to be understood that the above-described embodiments are illustrative of only a few of the many possible specific embodiments of the invention. Numerous and varied other arrangements can be made by those skilled in the art without departing from the spirit and scope of the invention.

Claims

1. A dielectric material comprising $(Ta_2O_5)_{1-x}(TiO_2)_x$ where $0.03 \leq x \leq 0.4$ and the dielectric constant of said material measured at 20°C and 1 MHz is greater than that of undoped Ta_2O_5.

2. The dielectric material of claim 1 wherein $0.05 \leq x \leq 0.15$.

3. A capacitor comprising a pair of conductive electrodes and, disposed between said electrodes, a layer of $(Ta_2O_5)_{1-x}(TiO_2)_x$ where $0.03 \leq x \leq 0.4$.

4. The capacitor of claim 3 wherein $0.05 \leq x \leq 0.15$.

FIG. 1

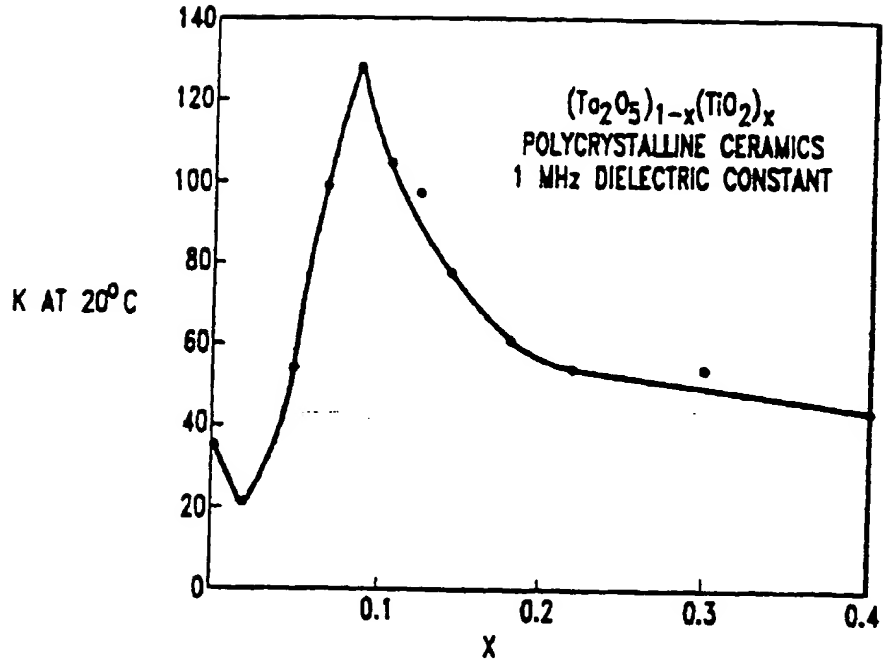

$(Ta_2O_5)_{1-x}(TiO_2)_x$
POLYCRYSTALLINE CERAMICS
1 MHz DIELECTRIC CONSTANT
K AT 20°C
0
20
40
60
80
100
120
140
0.1
0.2
0.3
0.4
X

FIG. 2

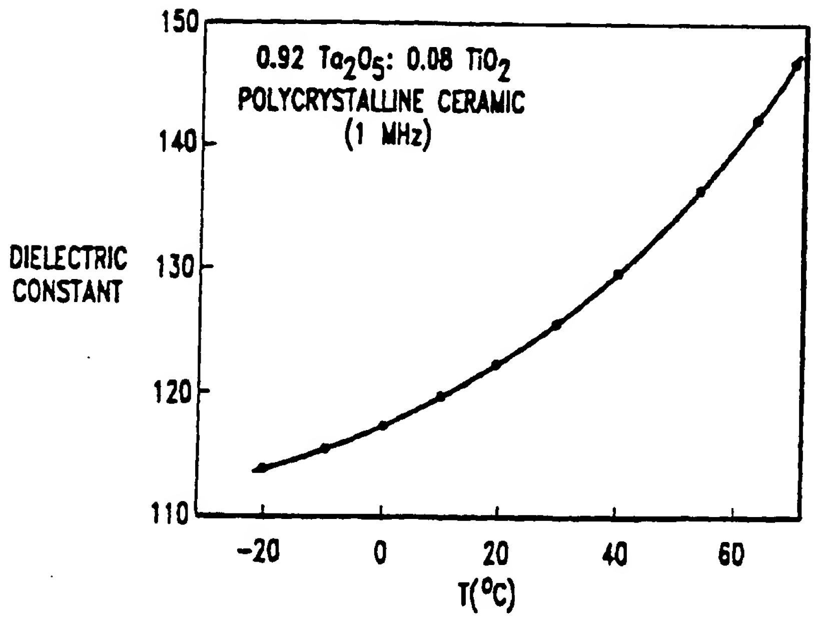

0.92 Ta_2O_5: 0.08 TiO_2
POLYCRYSTALLINE CERAMIC
(1 MHz)
DIELECTRIC CONSTANT
110
120
130
140
150
-20
0
20
40
60
T(°C)

FIG. 3

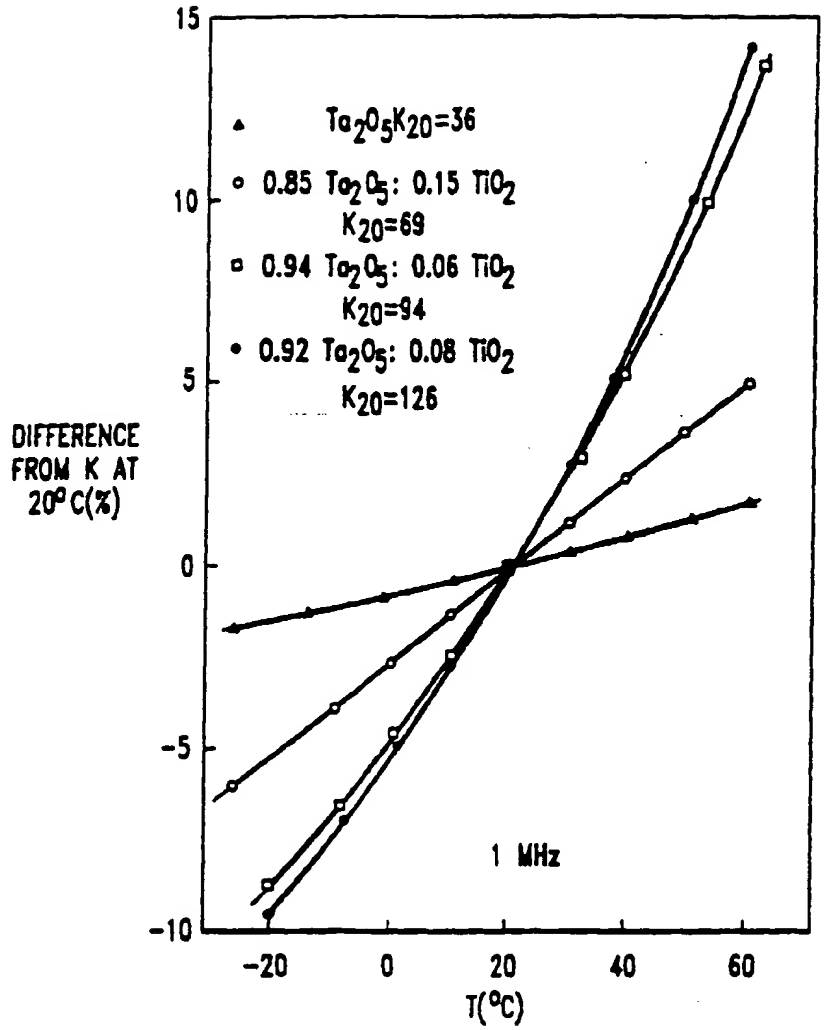
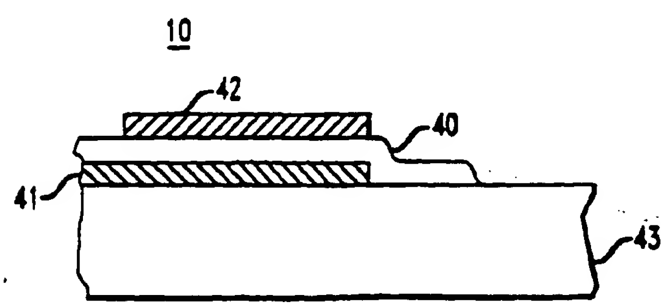

15
10
5
0
-5
-10
DIFFERENCE FROM K AT 20°C(%)
$Ta_2O_5 K_{20}=36$
$0.85\ Ta_2O_5: 0.15\ TiO_2$ $K_{20}=69$
$0.94\ Ta_2O_5: 0.06\ TiO_2$ $K_{20}=94$
$0.92\ Ta_2O_5: 0.08\ TiO_2$ $K_{20}=126$
1 MHz
-20
0
20
40
60
T(°C)

FIG. 4


10
42
40
41
43

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4079

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P,X	NATURE, vol. 377, no. 6546, 21 September 1995, UK, pages 215-217, XP002015101 CAVA R F ET AL.: "Enhancement of the dielectric constant of Ta2O5 through substitution with TiO2" * the whole document *	1-4	H01G4/10
A	EP-A-0 210 033 (SONY CORPORATION) 28 January 1987 * page 1, line 30 - page 2, line 3 * * page 2, line 10 - line 22 *	1-4	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
H01G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	3 October 1996	Goossens, A

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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